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Effects of carbon dioxide (CO_2) content of the air on the response of flame photometric sulfur gas analyzers of two types, the Tracor model 270 HA sulfur chromatograph and the Meloy model SA 185 total sulfur analyzer, were studied. These analyzers were used in the Regional Air Monitoring System (RAMS). For each instrument, measurements were made to determine response to a matrix of five CO_2 levels and three sulfur dioxide (SO_2) levels. Measurements were also made of CO_2 concentrations in the influent to and effluent from heatless air dryers providing zero air for calibration at the RAMS stations.

Little effect on the Tracor response to increased CO_2 was detected on either the SO_2 or total sulfur channel. The Meloy response was a suppressing effect of CO_2 which was linear over the values measured, averaging about a 20% suppression at the highest CO_2 level used (370ppm). The percentage suppression was independent of SO_2 concentration and of detector flame hydrogen flow rate. The zero air contained varying amounts of CO_2, apparently somewhat dependent on scrubber column packing and operating parameters, slightly dependent on influent CO_2 content, and not dependent on relative humidity. Because of the many RAMS component changes carried out during the period of measurements, detailed, site-specific corrections to the Meloy readings for the effects of CO_2 suppression would not be reliable and should not be made.

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Carbon Dioxide Effects on RAMS Sulfur Monitors

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REGIONAL AIR POLLUTION STUDY
Carbon Dioxide Effects on RAMS Sulfur Monitors

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ABSTRACT

Data has been collected to verify and quantify the effect of sample carbon dioxide content on the response of flame photometric sulfur gas analyzers of two types, the Tracor model 270HA sulfur gas chromatograph and the Meloy model SA 185 total sulfur analyzer. These analyzers were utilized in the Regional Air Monitoring System (RAMS).

The effectiveness of the RAMS heatless air drier in removing carbon dioxide from ambient air during the zero air generation process has been investigated. The effects of variables such as atmospheric moisture, ambient carbon dioxide concentration and dryer material have also been determined.

A wet chemical analytical technique has been refined and adapted for the determination of ambient carbon dioxide. The method is valid down to a concentration of 10 ppm. The technique has been validated utilizing NBS Standard Reference Material gases.

The diurnal variability of ambient carbon dioxide concentration at an urban location has been determined with data taken for four individual 24-hour periods. Atmospheric stability for each sampling period was determined with upper air soundings.

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1.0 INTRODUCTION

Data taken by the Rockwell International Air Monitoring Center, Research Triangle Institute and others have shown that carbon dioxide can be a suppressive interferent in the determination of gaseous sulfur compounds by the flame photometric technique. Differences in response of up to 20% have been reported for sample CO_2 concentration differences of zero to 360 ppm.

Calibration techniques employed in the Regional Air Monitoring System (RAMS) and other air monitoring programs utilize pollutant-free air (zero air) as a diluent for permeation tube effluent and compressed gas standards. The purification methods generally used to obtain this zero air frequently deplete its CO_2 content. The use of this CO_2 deficient air to determine instrument calibrations can result in the establishment of erroneous calibration coefficients which can lead to the understatement of ambient sulfur gas concentrations. The primary objective of this experimental work was to quantitatively determine the magnitude of this suppressive effect. Effort was also expended to determine the possible effect of instrument type and operational variables on this suppression.

Two types of sulfur gas analyzers were used in the RAMS network, the Tracor model 270HA sulfur gas chromatograph and the Meloy model SA 185 total sulfur analyzer. The effect of sample CO_2 content on the response of each has been investigated.

The RAMS station gas analyzer calibration system utilizes zero air which is generated by a heatless air dryer and purification device. Preliminary analysis for the CO_2 content of the zero air effluent from this station zero air generation system performed by Research Triangle Institute (RTI) has indicated that the percentage of ambient level CO_2 (nominally 350 to 370 ppm) which is removed by different systems within the RAMS network varies from 30 to 100 percent. The station zero air generation system influent and

effluent have been analyzed daily at three RAMS stations for a twenty day period to determine the system scrubbing efficiency and to attempt to elucidate the factors, such as temperature and atmospheric moisture content, which might effect this scrubbing efficiency.

Because of the possible effect of the ambient CO_2 concentration variability on the reported sulfur gas concentration and the zero air CO_2 content, ambient air samples taken every four hours for four individual diurnal cycles were analyzed for CO_2 content.

2.0 RAMS ZERO AIR SYSTEM CO_2 SCRUBBING EFFICIENCY

2.1 EXPERIMENTAL METHODS

Determinations of CO_2 in both influent and effluent of the heatless dryer scrubbing system were performed to determine the efficiency of this device for CO_2 removal. These determinations were made daily at each of the three stations involved in this study from 4 May 1977 to 24 May 1977, inclusive. These analyses were performed by bubbling the sample air through gas washing bottles (bubblers) which were prepared at the central facility, sealed, and transported to the station for sampling. After sampling, the bubblers were resealed and returned to the central facility for same-day analysis.

The heatless dryer influent sample was obtained by pumping the inside air from the shelter through a calcium sulfate drying cartridge (indicating drierite), a mass flow meter, and then to the analytical absorption device (bubbler). The drying cartridge was necessary because the moisture content of the sample will effect its thermal conductivity and hence the ability to be volumetrically measured with a mass flow meter. The heatless dryer effluent was sampled from the station calibration system through an existing test port on the calibration panel which allows pressurized zero air to be sampled. This sample was volumetrically measured with the same mass flow meter.

The relative humidity of the zero air system influent was measured by taking a psychrometer reading inside the shelter at the time of CO_2 sampling. The enclosure containing the station zero air generation system is ventilated with the air conditioning system output. The station inside air is, therefore, representative of the zero air system influent.

Table 1 contains the results of this study. Those days listed as "not available", were due to problems at the RAMS site heatless dryer or computer. Duplicate samples were collected on 18 May 1977 and 22 May 1977 from site

TABLE 1. CO_2 CONTENT OF AMBIENT AND RAMS ZERO AIR

DATE	SITE	AMBIENT AIR CO_2 TIME (CST)	ZERO AIR CO_2 TIME (CST)	RELATIVE HUMIDITY	AMBIENT TEMP. (°C)	AMB. AIR CO_2 (ppm) (average of 2 analyses)	ZERO AIR CO_2 (ppm) (average of 2 analyses)
5/4/77	111	1145	1225	63%	27.5	359	54
5/4/77	107	0730	0805	86%	17.8	440	16
5/4/77	106	0915	1005	74%	22.7	327	105
5/5/77	111	1150	1320	62%	21.1	360	49
5/5/77	107	0655	0740	86%	21.1	441	14
5/5/77	106	0910	1000	64%	18.8	332	95
5/6/77	111		Not Available				
5/6/77	107	0755	0840	71%	14.9	454	16
5/6/77	106	1159	1134	60%	9.9	375	121
5/7/77	111	1016	1102	61%	10.2	487	51
5/7/77	107	0705	0755	64%	12.0	508	21
5/7/77	106		Not Available				
5/8/77	111	1126	1215	50%	18.6	455	16
5/8/77	107	0704	0750	49%	21.9	510	21
5/8/77	106	0924	1005	53%	17.2	347	110
5/9/77	111	1041	1134	33%	17.5	398	51
5/9/77	107	0657	0733	32%	17.8	422	21
5/9/77	106	0843	0920	28%	20.6	379	118
5/10/77	111	1128	1215	29%	23.3	400	45
5/10/77	107	0706	0750	29%	20.0	457	40
5/10/77	106	0908	0946	31%	21.1	398	95
5/11/77	111	1151	1258	35%	22.0	403	46
5/11/77	107	0730	0810	43%	17.8	445	22
5/11/77	106	0845	0924	37%	21.4	424	133
5/12/77	111	1133	1210	35%	22.5	398	46
5/12/77	107	0712	0750	43%	16.9	517	18
5/12/77	106	0909	0945	43%	20.0	360	118
5/13/77	111	1136	1241	45%	25.5	372	50
5/13/77	107	0726	0823	46%	19.7	454	40
5/13/77	106	0940	1020	51%	23.0	340	145

(continued)

TABLE 1 (continued)

DATE	SITE	AMBIENT AIR CO_2 TIME (CST)	ZERO AIR CO_2 TIME (CST)	RELATIVE HUMIDITY	AMBIENT TEMP. (°C)	AMB. AIR CO_2 (ppm) (average of 2 analyses)	ZERO AIR CO_2 (ppm)
5/14/77	111	0959	1108	46%	26.5	349	49
5/14/77	107		Not Available				
5/14/77	106	0747	0842	47%	25.0	371	148
5/15/77	111	0922	1015	47%	27.5	358	49
5/15/77	107		Not Available				
5/15/77	106	0717	0812	53%	24.5	354	194
5/16/77	111	1200	1238	47%	27.5	355	46
5/16/77	107		Not Available				
5/16/77	106	0915	0952	50%	27.5	355	151
5/17/77	111	1213	1307	47%	27.5	348	47
5/17/77	107	0738	0835	43%	26.5	379	26
5/17/77	106	1005	1049	52%	27.0	344	99
5/18/77	111	1158	1245	47%	27.5	394	34
5/18/77	107	0723	0825	47%	25.5	403	29
5/18/77	106	1006	1049	59%	25.0	337	115
5/18/77	107	0756	0853	Duplicate Sample		390	113
5/19/77	111	1100	1135	44%	27.5	371	32
5/19/77	107	0739	0815	51%	25.5	423	22
5/19/77	106	0924	1000	51%	25.5	346	118
5/20/77	111	1144	1226	46%	27.0	339	45
5/20/77	107	0726	0810	46%	26.5	390	12
5/20/77	106	0928	1012	49%	26.5	348	107
5/21/77	111	0853	0945	53%	27.5	363	49
5/21/77	107	1105	1143	40%	28.5	371	14
5/21/77	106	0707	0746	40%	23.5	364	127
5/22/77	111	1245	1330	42%	26.0	360	46
5/22/77	107	0748	0823	47%	25.5	363	8
5/22/77	106	0934	1049	45%	24.0	357	117
5/22/77	106	1009	1123	Duplicate Sample		358	111
5/23/77	111	1430	1516	48%	28.0	361	46
5/23/77	107	0947	1023	56%	24.5	378	13
5/23/77	106	1253	1331	38%	31.5	366	51
5/24/77	111	1143	1239	58%	26.5	349	45
5/24/77	107	0720	0807	56%	24.5	398	11
5/24/77	106	0930	1031	59%	24.5	380	100

107 and 106, respectively. These duplicates were taken and analyzed to establish a confidence level on the accuracy of this sampling method.

The two RAMS sites that gave the most divergent CO_2 concentrations in the station zero air were sites 107 and 106. Sites 107 and 106 average 20 and 118 ppm CO_2, respectively. To determine the cause of this difference, the two heatless dryer scrubber columns from both sites were removed and disassembled. The scrubber from 106 was found to contain only activated charcoal. That from site 107 contained a layer of 200 ml of Linde Molecular Sieve 5A, with the remaining 800 ml of column consisting of activated charcoal. This lends evidence that Mole Sieve 5A has a retentive effect on CO_2.

Linde, in their materials catalogue, contend that Mole Sieve 5A will effectively remove any molecule with an effective diameter of 5 angstroms or less. CO_2 has an effective diameter of less than 4 angstroms.

Other parameters for the scrubbing efficiency of the heatless dryers are the pressure at which scrubbing occurs, amount of air scrubbed, cycle time for each half of the dryer, and the age of the column materials. Because of time and material shortages, no attempt was made to determine if any other column packings would have a decreased affinity for CO_2 (e.g., activated alumina), and yet generate air free of pollutants and moisture.

2.2 CONCLUSIONS

From this study it can be concluded that the heatless dryers containing activated charcoal do remove varying amounts of the CO_2 from the ambient air influent. The amount of CO_2 scrubbed is enhanced by the added presence of Linde Molecular Sieve 5A in the dryer. Other factors that are probably involved, but were not tested, are the pressure at which the air is scrubbed by the dryer and the total volume of air being withdrawn from the system at the time of sampling. Relative humidity does not appear to have any affect on the amount of CO_2 removed by the station zero air generation system.

3.0 EFFECT OF CARBON DIOXIDE ON MELOY AND TRACOR SULFUR GAS MEASUREMENTS

3.1 EXPERIMENTAL METHODS

To determine the effect of the CO_2 sample concentration on Meloy and Tracor response, span gas consisting of SO_2 concentration of 48 and 102 parts per billion (ppb) were prepared using 4, 46, 92, 188 and 370 ppm CO_2.

The span gas samples were generated utilizing the portable dynamic dilution system which was used for RAMS quality assurance field audits. The source of SO_2 is a National Bureau of Standards (NBS) permeation tube (elution rate 0.267 µl/min.) in a temperature controlled environment. The various CO_2 concentrations were generated by attachment of the required CO_2 spiked gas cylinder to the dilution gas input of the calibrator. Figure 1 gives a representation of the calibration system used to perform this test.

This test was done on the rack mounted Tracor at site 106 and the rack mounted Meloy instruments at sites 107 and 111, with a duplicate test at site 111. All output data were generated from the RAMS data acquisition system and recorded in Tables 2-6.

To determine the effect of flame support hydrogen flow on the CO_2 interference, the tests mentioned previously in this section were repeated using varied hydrogen flow rates. These rates and their corresponding results are also listed in Tables 2-6.

3.2 CONCLUSIONS

Results from Meloy sites 107 and 111 indicate that there is a total sulfur gas response supression, ranging up to 20% for varied ambient CO_2 concentrations using constant sulfur gas concentrations. These results show that the supression is not a function of sulfur gas present, but that some slight variation does occur with varied hydrogen flows used to support the detection flame. The factory recommended hydrogen flow rate of 52 ml/min.

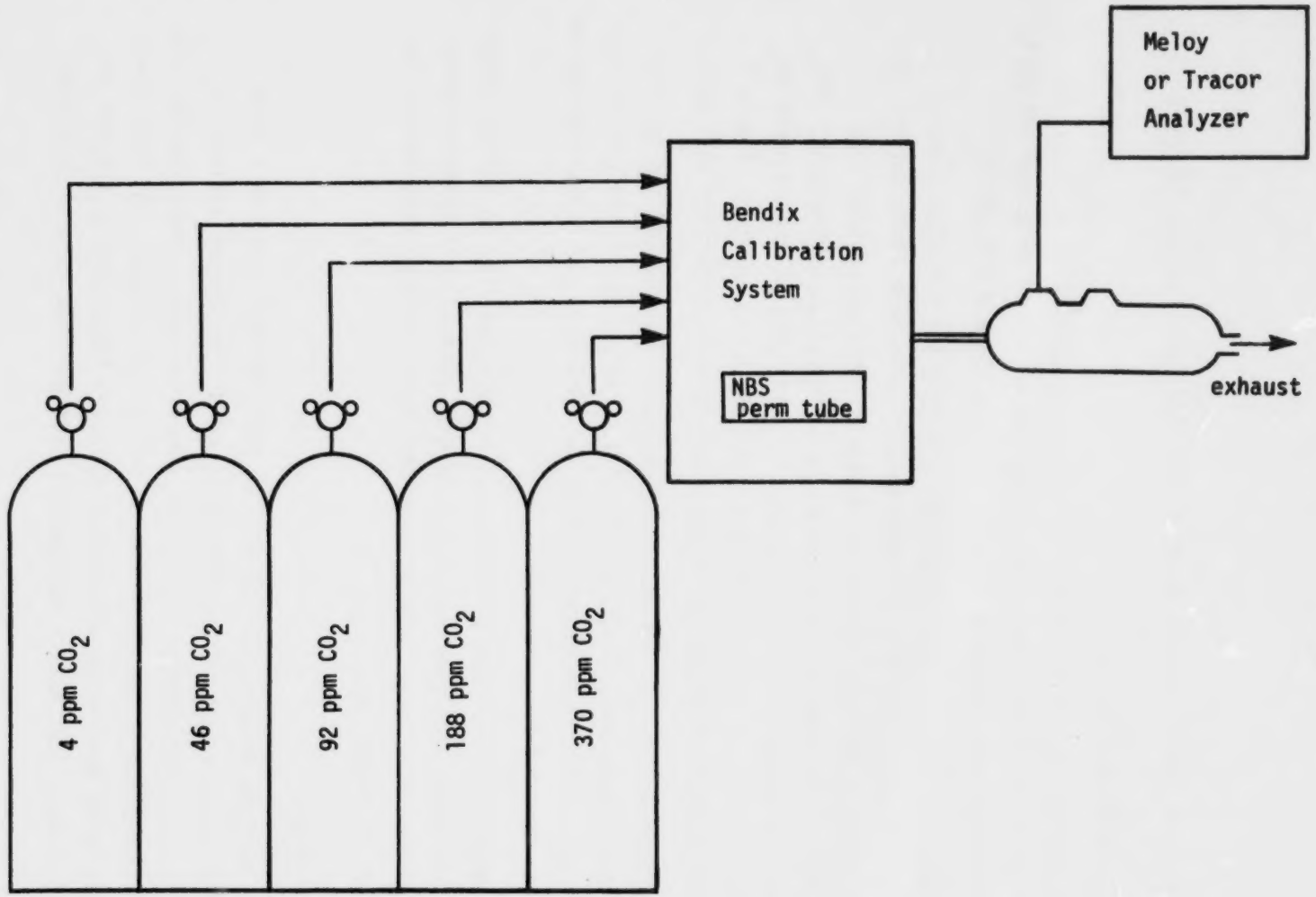

FIGURE 1. CALIBRATION GAS CONFIGURATION

TABLE 2. TRACOR SO_2 RESPONSE - SITE 106

(Run on 6/2/77)

CO_2 CONC. (ppm)	INSTRUMENT RESPONSE IN VOLTS			INSTRUMENT RESPONSE IN ppb SO_2		
	0 ppb SO_2	48 ppb SO_2	102 ppb SO_2	0 ppb SO_2	48 ppb SO_2	102 ppb SO_2
		Run at 29 lbs H_2 (54.5 ml/min)				
4	0.068	0.896	1.770	2.4	33.9	67.1
46		0.896	1.738	-	33.9	65.9
92		0.879	1.704	-	33.2	64.6
188		0.896	1.789	-	33.9	67.8
370	0.071	0.896	1.790	2.5	33.9	67.8
		Run at 31 lbs H_2 (64.9 ml/min)				
4	0.122	0.947	1.838	4.5	35.8	69.7
46		1.047	1.990	-	39.6	75.4
92		1.030	2.039	-	39.0	77.3
188		1.013	1.855	-	38.3	70.3
370	0.088	0.896	1.704	3.2	33.9	64.6
		Run at 27 lbs H_2 (45.1 ml/min)				
4	0.088	0.862	1.670	3.2	32.6	63.3
46		0.913	1.719	-	34.5	65.1
92		0.879	1.636	-	33.2	62.0
188		0.896	1.704	-	33.9	64.6
370	0.130	1.030	1.704	4.8	39.0	64.6

Transfer equation: SO_2 (ppm) = 0.0380 (v) - 0.00018.

TABLE 3. TRACOR TOTAL SULFUR RESPONSE - SITE 106

(Run on 6/2/77)

CO_2 CONC. (ppm)	INSTRUMENT RESPONSE IN VOLTS			INSTRUMENT RESPONSE IN ppb TS*		
	0 ppb SO_2	48 ppb SO_2	102 ppb SO_2	0 ppb SO_2	48 ppb SO_2	102 ppb SO_2
		Run at 29 lbs H_2 (54.5 ml/min)				
4	0.042	0.900	1.816	1.4	33.0	66.9
46		0.920	1.799	-	33.8	66.2
92		0.901	1.743	-	33.1	64.2
188		0.884	1.760	-	32.5	64.8
370	0.173	0.864	1.799	6.2	31.7	66.2
		Run at 31 lbs H_2 (64.9 ml/min)				
4	0.061	0.977	1.929	2.1	35.9	71.0
46		1.069	1.929	-	39.3	71.0
92		1.013	2.041	-	37.2	75.2
188		0.994	1.836	-	36.5	67.6
370	0.134	0.884	1.667	4.8	32.5	61.4
		Run at 27 lbs H_2 (45.1 ml/min)				
4	0.098	0.920	1.760	3.4	33.8	64.8
46		0.957	1.799	-	35.0	66.2
92		0.901	1.687	-	33.1	62.1
188		0.938	1.760	-	34.5	64.8
370	0.190	0.920	1.743	6.8	33.8	64.2

Transfer equation: TS* (ppm) = 0.03692 (v) - 0.000177.

*SO_2 Equivalent.

TABLE 4. MELOY TOTAL SULFUR RESPONSE - SITE 107

(Run on 6/11/77)

CO_2 CONC. (ppm)	INSTRUMENT RESPONSE IN VOLTS			INSTRUMENT RESPONSE IN ppb TS*		
	0 ppb SO_2	48 ppb SO_2	102 ppb SO_2	0 ppb SO_2	48 ppb SO_2	102 ppb SO_2
			Run at 52 ml/min H_2			
4	0.210	1.237	2.315	-4.4	45.3	97.4
46		1.168	2.219	-	41.9	92.8
92		1.139	2.191	-	40.5	91.4
188		1.079	2.081	-	37.6	86.1
370	0.256	1.009	1.900	-2.2	34.2	77.3
			Run at 48 ml/min H_2			
4	0.257	1.195	2.236	-2.2	43.2	93.6
46		1.181	2.238	-	47.6	93.7
92		1.099	2.118	-	38.6	87.9
188		1.029	2.081	-	35.2	86.1
370	0.255	0.973	1.843	-2.3	32.5	74.6
			Run at 56 ml/min H_2			
4	0.101	1.107	2.094	-9.7	39.0	86.7
46		1.100	2.085	-	38.6	86.3
92		1.081	2.089	-	37.7	86.5
188		0.993	1.842	-	33.5	74.5
370	0.121	0.899	1.790	-8.7	28.9	72.0

Transfer equation: TS* (ppm) = 0.048393 (v) - 0.014615.

*SO_2 Equivalent.

TABLE 5. MELOY TOTAL SULFUR RESPONSE - SITE 111

(Run on 6/12/77)

CO_2 CONC. (ppm)	INSTRUMENT RESPONSE IN VOLTS			INSTRUMENT RESPONSE IN ppb TS*		
	0 ppb SO_2	48 ppb SO_2	102 ppb SO_2	0 ppb SO_2	48 ppb SO_2	102 ppb SO_2
			Run at 52 ml/min H_2			
4	0.061	1.167	2.266	0.5	46.3	91.8
46		1.127	2.165	-	44.7	87.6
92		1.116	2.150	-	44.2	87.0
188		1.045	2.046	-	41.3	82.7
370	0.083	0.977	1.865	1.4	38.4	75.2
			Run at 48 ml/min H_2			
4	0.159	1.179	2.219	4.6	46.8	89.9
46		1.152	2.202	-	45.7	89.2
92		1.079	2.092	-	42.7	84.5
188		1.009	2.058	-	39.8	83.2
370	0.144	0.942	1.804	4.0	37.0	72.7
			Run at 56 ml/min H_2			
4	-0.011	1.084	2.078	-2.5	42.9	84.0
46		1.077	2.061	-	42.6	83.3
92		1.052	2.058	-	41.6	83.2
188		0.977	1.926	-	38.4	77.7
370	0.066	0.874	1.760	0.7	34.2	70.9

Transfer equation: TS* (ppm) = 0.041355 (v) - 0.002018.

*SO_2 Equivalent.

TABLE 6. MELOY TOTAL SULFUR RESPONSE - SITE 111 (Duplicate)

(Run on 6/12/77)

CO_2 CONC. (ppm)	INSTRUMENT RESPONSE IN VOLTS			INSTRUMENT RESPONSE IN ppb TS*		
	0 ppb SO_2	48 ppb SO_2	102 ppb SO_2	0 ppb SO_2	48 ppb SO_2	102 ppb SO_2
			Run at 52 ml/min H_2			
4	0.062	1.166	2.265	0.5	46.2	91.6
46		1.130	2.166	-	44.7	87.6
92		1.116	2.171	-	44.1	87.8
188		1.044	2.042	-	41.2	82.4
370	0.082	0.979	1.861	1.4	38.5	74.9
			Run at 48 ml/min H_2			
4	0.158	1.177	2.221	4.5	46.7	89.8
46		1.145	2.200	-	45.3	89.0
92		1.077	2.095	-	42.5	84.6
188		1.088	2.055	-	43.0	83.0
370	0.139	0.945	1.805	3.7	37.1	72.4
			Run at 56 ml/min H_2			
4	-0.011	1.079	2.077	-2.5	47.6	83.9
46		1.075	2.060	-	42.4	83.2
92		1.050	2.059	-	41.4	83.1
188		0.977	1.925	-	38.4	77.6
370	0.061	0.877	1.761	0.5	34.2	70.8

Transfer equation: TS* (ppm) = 0.041355 (v) - 0.002018.

*SO_2 Equivalent.

was identical for each Meloy. By changing this flow rate to 56 and 48 ml/min., no appreciable improvement in response versus CO_2 concentration was found.

Analysis of the data from the Tracor at site 106 indicated no change in instrument response due to varied sample CO_2 concentration, at either 48 or 102 ppb SO_2. This held true for both the total sulfur and the SO_2 output channels. There was a $\pm$ 2% variation in response for both channels, but this did not fit into any progression concerning CO_2 concentration. An increase in this variation did occur when the instrument was operated at both a higher and lower hydrogen flow rate. As before, the variation was in no orderly progression and can be attributed to instrument noise due to operation at the extreme hydrogen flow rates.

It was expected that the Meloy would be more sensitive to ambient CO_2 concentrations. The Meloy instrument draws in between 50 and 60 ml/min. of sample air for analysis and to support the hydrogen detector flame. This air is subject to variation in CO_2 concentration depending on its source (i.e. ambient or station zero air). The Tracor injects only a 5 ml sample per injection. This amount is dwarfed in the hydrogen flame by 100 to 120 ml/min. of air from the RAMS air purification system. As the heatless dryer generates air of a generally constant CO_2 concentration, the changes in instrument sensitivity due to variations in ambient sample CO_2 concentration are minimized.

4.0 SIMULTANEOUS OPERATION OF MELOY AND TRACOR INSTRUMENTS

The comparability of ambient air sulfur gas content reported by the Meloy and Tracor sulfur gas analyzers was investigated by operating both instruments at RAMS station 106, 107, and 111. Stations 107 and 111 each have normally installed Meloy instruments. These stations each were equipped with a Tracor instrument mounted on the station workbench. Station 106 has a normally installed Tracor instrument and an auxiliary Meloy was installed at this site. Each of the auxiliary instruments derived its ambient air and calibration gas sample identically to the station instument. A spare run/calibrate valve was electrically connected to the sulfur analyzer run/calibrate signal for the auxiliary instrument, allowing the selection of either the ambient air sample manifold or the calibration manifold as the sample source under either station computer or manual control. The signal output from the auxiliary instruments was connected to the RAMS station data acquisition system via unused signal input channels.

From 4 May 1977 to 24 May 1977, inclusive, both station and auxiliary sulfur analyzers were zeroed/spanned manually for the 20 days of this test. The total sulfur parameter for the Meloy instruments and the total sulfur and sulfur dioxide parameters for the Tracor instruments were subjected to this daily calibration only on the most sensitive operating ranges (0-0.2 ppm). This calibration was in addition to the normal computer executed zero/span each evening. The manually executed calibrations were performed each data at approximately the same hour and immediately following the sampling activities for the zero air CO_2 concentration. Data obtained from these calibrations were derived from the remote station data acquisition system and were manually recorded. Slope and intercept values were computed manually and these calibration values were input to the RAMS central computer for conversion of level 1 to level 2 data exclusive for this study.

The central computer was programmed to extract both station and

auxiliary instrument data from the level 1 tape file, and the data was placed on a special tape file to be processed to level 2 (engineering unit) using the manually input calibration constants. The level 2 data in this file had only lower detection limit validation checking. All other validation was manually performed. An attempt was made to analyze the data; however, the contract effort was terminated before any conclusions were reached regarding the comparability of the Meloy and Tracor analyzers.

5.0 DIURNAL CO_2 SAMPLING

To determine the fluctuation of ambient CO_2 concentration, diurnal sampling was conducted for four 24 hour periods at site 106. These samples were collected every 4 hours and analyzed within the hour. Samples were gathered and analyzed per the procedures in Appendix A. These results are presented in Table 7.

Results range from a high CO_2 reading of 409 ppm CO_2 at 0215 central standard time on 21 May 1977 to a low of 322 ppm CO_2 at 1344 on 24 May 1977. A general tendency seen from these results is the increase in CO_2 concentration during hours of darkness. Bacterial decay of plant materials on the surface is most likely the predominant source of atmospheric CO_2. The increases in CO_2 concentration observed during hours of darkness are attributed to this constant source coupled with the reduced vertical mixing experienced during nighttime hours.

TABLE 7. DIURNAL CO_2 TEST RESULTS - SITE 106

DATE	TIME*	CO_2 CONC. (ppm)
1st DIURNAL PERIOD		
5/20/77	0928	348
5/20/77	1412	337
5/20/77	1815	347
5/20/77	2215	363
5/21/77	0215	409
5/21/77	0707	363
2nd DIURNAL PERIOD		
5/24/77	0930	351
5/24/77	1344	322
5/24/77	1800	338
5/24/77	2200	352
5/25/77	0200	373
5/25/77	0600	403
3rd DIURNAL PERIOD		
5/31/77	1000	371
5/31/77	1400	369
5/31/77	1800	354
5/31/77	2200	360
6/1/77	0200	367
6/1/77	0600	366
4th DIURNAL PERIOD		
6/7/77	1030	357
6/7/77	1430	341
6/7/77	1830	369
6/7/77	2230	371
6/8/77	0230	371
6/8/77	0630	344

* All time is reported in central standard time.

6.0 QUALITY ASSURANCE

A Bendix dynamic calibrator was used in performing the work described in section 3.1. This device was calibrated prior to and checked after its use by the positive soap film displacement technique. No discrepancy was found between these two calibrations.

The permeation device used in this section to generate SO_2, was a National Bureau of Standards permeation tube, calibrated at 0.267 µl/min.

APPENDIX A

PROCEDURES FOR THE DETERMINATION OF CARBON DIOXIDE IN AIR

A.1 INTRODUCTION

In compliance with Task Order 121, an analytical method was developed for the analysis of carbon dioxide (CO_2) in air samples. It was necessary that this method be accurate, reproducible, relatively simple, have an analytical range between 0 and 550 parts per million (ppm) CO_2, and not require a large capital expenditure. A literature search revealed an analytical method for CO_2 using the reaction between CO_2 and barium hydroxide ($Ba(OH)_2$).[1,2]

The following sections detail the analysis, sampling, quality assurance, and other related procedures used for these CO_2 analyses.

A.2 SUMMARY

The method which was used for the determination of CO_2, involves the dissolution and reaction of CO_2 in a known amount of a standard barium hydroxide solution [$Ba(OH)_2$]. An acid-base titration of the unreacted $Ba(OH)_2$ was then performed with a known concentration of oxalic acid [$(COOH)_2$]. These factors along with the known volume, at standard temperature and pressure (STP), of sample passed through the absorbing solution, determined the CO_2 concentration in parts per million.

The reaction between CO_2 and $Ba(OH)_2$ absorbing solution is given by the following equation:

$$CO_2 + Ba(OH)_2 \rightarrow BaCO_3 \downarrow + H_2O$$

The titration of the remaining base with oxalic acid is given by the following equation:

$$Ba(OH)_2 + (COOH)_2 \rightarrow Ba(COO)_2 + 2H_2O$$

Tests were run using certified standards to insure the accuracy of this method. These tests proved this method accurate to $\pm$ 3 ppm.

Because the concentrations of CO_2 found during these experiments were substantially larger than those of any interfering gases (e.g. SO_2, which occur at maximum concentrations of less than 0.5 ppm), no special gas traps or correction factors were needed.

A.3 ANALYTICAL AND SAMPLING PROCEDURES FOR CO_2 DETERMINATION

The following paragraphs describe the sequence of preparations required for carbon dioxide (CO_2) determination in ambient, station zero, and CO_2 spiked standard air.

A.3.1 PREPARATION OF REAGENTS

A.3.1.1 Preparation of 0.1 molar (M) oxalic acid stock solution

Dilute 12.607 gm oxalic acid [$(COOH)_2 \cdot 2H_2O$][1] to 1 litre using freshly deionized water in a volumetric flask.[2] Transfer this solution to a stoppered glass bottle.[3]

A.3.1.2 Preparation of 0.005 M oxalic acid titration solution

Pipette 50 ml of 0.1 M oxalic acid stock solution into a volumetric flask and dilute to 1 litre using freshly deionized water. Transfer this solution to a stoppered glass bottle.[3]

A.3.1.3 Preparation of 0.1 M barium hydroxide [$Ba(OH)_2$] stock solution

Dissolve 31.548 gm of $Ba(OH)_2 \cdot 8H_2O$ in a volumetric flask and dilute to 1 litre using freshly deionized water. Due to carbonates and other impurities normally found in crystaline $Ba(OH)_2$, the resulting turbid

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1. Oxalic acid is used as a standard for determining CO_2 because it is available in a purity of > 99.99% and a stable hydrated form.
2. Freshly deionized water is free of any carbonates or carbon dioxide.
3. As oxalic acid is used as an analytical standard material, these pipettings and weighings need to be exact. The oxalic acid is A.C.S. grade in crystalline form.

solution requires filtration prior to storage in a glass stoppered bottle.[4]

A.3.1.4 Preparation of 0.01 M $Ba(OH)_2$ absorption solution

Pipette 100 ml of 0.1 M $Ba(OH)_2$ stock solution into a volumetric flask and dilute to 1 litre using freshly deionized water. Transfer this solution to a stoppered glass bottle.[4,5]

A.3.2 PREPARATION OF A CO_2 GAS SAMPLING BOTTLE

Pipette 100 ml of 0.01 M $Ba(OH)_2$ absorbing solution into a 250 ml fritted glass gas washing bottle (bubbler).[6] Add 10 drops (0.5 ml) of 1-butanol to this solution.[7] Plug both ends of the bubbler to preclude any ambient CO_2 contamination.

A.3.3 SAMPLE GATHERING

Samples to be analyzed for CO_2 are bubbled through the CO_2 bubbler at a rate of 1 litre per minute (l/min) at standard temperature and pressure (STP) for 30 minutes.

The rate of 1 l/min was chosen as close to the maximum allowable rate without an absorption fluid loss due to overflow. 30 minutes was chosen as a sampling time in order that a mass of CO_2 in excess of what could be

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4. Any pipetting or weighing need not be exact. Precise standardization will be done with the 0.005 M oxalic acid solution.

5. Unlike the acidic oxalic acid solutions where CO_2 is insoluable, CO_2 is very soluable and reactive in the $Ba(OH)_2$ working and absorbing solution. Care is required to minimize ambient CO_2 contamination.

6. The exact amount of absorbing solution used to charge a bubbler is critical. While any known amount could be used, 100 ml was used as it filled the bubbler above the fritted glass and was not subject to overflow during sampling.

7. 1-Butanol is used to relieve surface tension in the $Ba(OH)_2$ solution and generate a 10 cm bubble column to facilitate CO_2 absorption.

absorbed would not be sampled.[8] Ambient CO_2 sampling required the use of a metal diaphram pump to force sample through the mass flow meter while sampling station zero air required only a pressure regulator. This regulator was used to reduce the station zero air pressure from 70 lbs to the 10 lbs needed for use with the mass flow meter. Figure A.1 illustrates the sampling train used.

A.3.4 SAMPLE ANALYSIS

The exact molarity of unreacted $Ba(OH)_2$ absorbing solution used to charge the CO_2 bubbler(s), is determined by pipetting 25 ml of the stock absorbing solution and titrating with 0.005 M oxalic acid. Two drops 1% thymolphthalein are used as an indicator, with the solution titrated from blue to colorless. The ml of oxalic acid used is recorded and later used for calculating CO_2 concentrations.

This procedure is repeated when titrating a reacted bubbler absorbing solution. As some of the barium carbonate ($BaCO_3$) precipitate formed by the $Ba(OH)_2$ reaction with CO_2 will enter into the titration, the titration should be performed slowly to enable a complete $Ba(OH)_2$ digestion from the precipitate by the oxalic acid. A reference titration proves very beneficial in determining the end point.[9]

It is preferable that no $BaCO_3$ precipitate enter the titration, but without the use of centrifuge, this is almost impossible. As $BaCO_3$ precipitate is soluable in acidic solutions, a loss of carbon dioxide is possible through a "fizzing-out" process if the end point of the titration has an acidic pH. Thymolphthalein is used as an indicator as its transition range is 9.3-10.5. The final end point for this titration is basic and allows no CO_2 loss through dissolution of the $BaCO_3$ precipitate.

All titrations were done using a 50 ml burette. By titrating 25 ml

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8. The maximum CO_2 concentration that may be used for these reagent and sampling parameters is 747 ppm CO_2.

9. A gas tube exhausting CO_2 free air in the titration flask proves beneficial in retarding ambient CO_2 interference. Ascarite efficiently absorbs all CO_2.

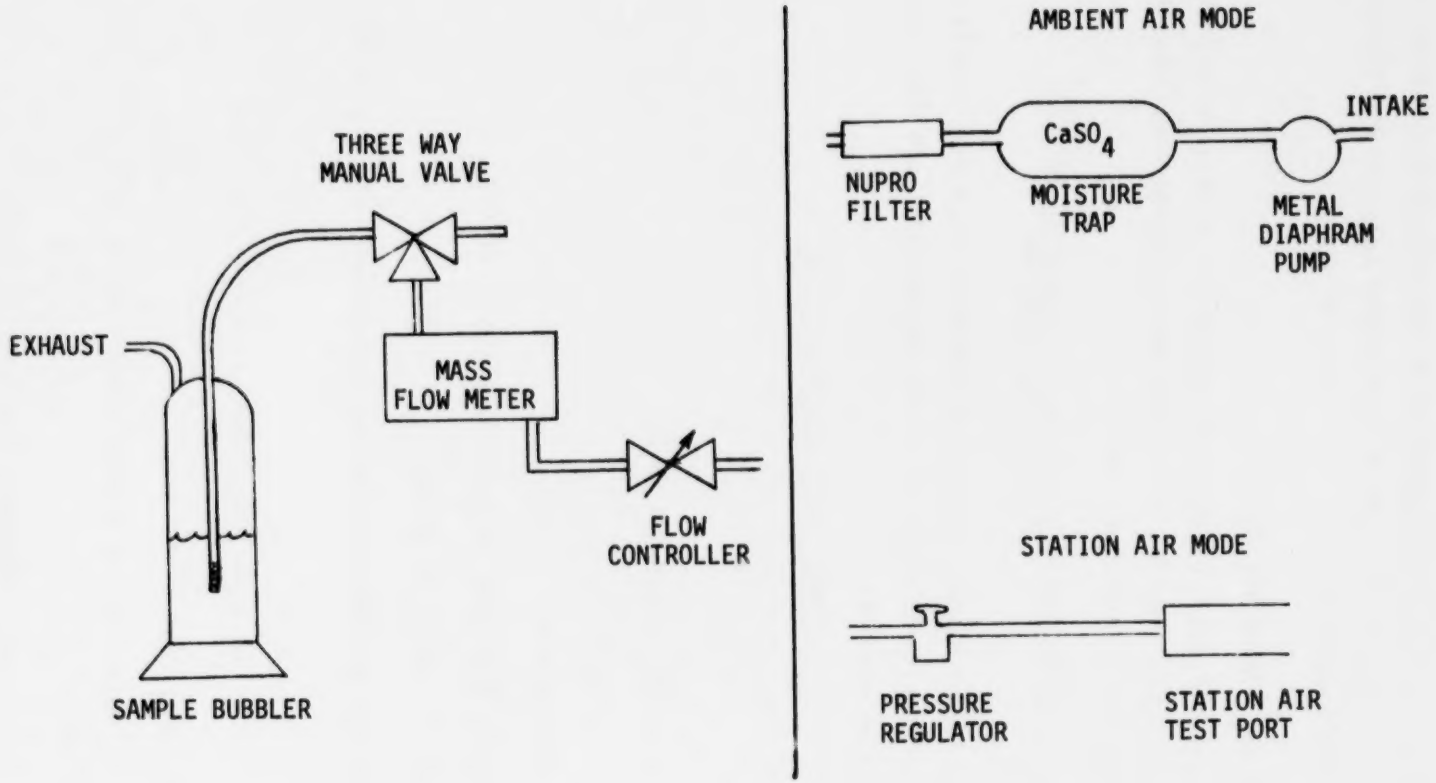

FIGURE A.1 CO_2 SAMPLING TRAIN

of absorbing solution, at twice the normality of the titrating solution, no need arose to use more than 50 ml 0.005 M oxalic acid solution and thusly no need to refill the burette with its associated errors.

A.3.5 CALCULATING CO_2 CONCENTRATIONS

From the amount of 0.005 M oxalic used to neutralize 25 ml unreacted $Ba(OH)_2$ absorbing solution (section A.3.4) and the following equation, the exact $Ba(OH)_2$ molarity was determined, where:

$$M\ Ba(OH)_2 = \frac{\text{ml of oxalic acid used x oxalic acid molarity}}{\text{ml of } Ba(OH)_2 \text{ titrated}}$$

From the molarity of $Ba(OH)_2$ and the amount of 0.005 M oxalic acid used to neutralize the absorbing solution in a used CO_2 bubbler (section A.3.4), the following equation applies:

$$A = \frac{22400\ (100 \times B - 4 \times C \times D)}{E}$$

where:

A = CO_2 conc. in the sample gas in ppm

B = $Ba(OH)_2$ molarity

C = oxalic acid molarity

D = ml of oxalic acid used in neutralization of $Ba(OH)_2$

E = amount of air sample in litres

This equation was derived from the reaction between CO_2 and $Ba(OH)_2$ where:

$$CO_2 + Ba(OH)_2 \rightarrow BaCO_3 \downarrow + H_2O$$

that CO_2 (gas) occupies 22.4 litres at STP;

and that a mole per mole reaction occurs between oxalic acid and $Ba(OH)_2$ during titration, where:

$$Ba(OH)_2 + (COOH)_2 \rightarrow Ba(COO)_2 + 2H_2O$$

The constants in the equation used to determine CO_2 concentration apply only if 100 ml of absorbing solution is used to charge a bubbler, and if 25 ml of this solution is titrated.

Experiments showed that approximately 0.5 ml of absorbing solution was lost for each 10 litres of sample collected. Allowing for the 0.5 ml added from the 1-butanol required, a correction (reduction) of 1% to the CO_2 concentration is required for a 30 litre sample.

A.3.6 CALIBRATION OF MASS FLOW METERS

A Tylan mass flow meter was used to measure the flow rate of sample through the CO_2 bubbler. This mass flow meter was calibrated for 1 l/min at STP and rechecked approximately once every week during the period of sampling. The original setting at the start of sampling was 0.164 volts and did not change during the period of use. On 31 May 1977 a Brooks mass flow controller was used with considerable success due to its incorporation of a flow controller. The Brooks mass flow controller proved much more stable at regulating a constant flow and in hindsight would have proved a better initial choice. The Brooks mass flow controller and Tylan mass flow meter were both calibrated against a 5 litre bubble tube. The setting of 0.352 volts for the Brooks at 1 l/min (STP) proved constant during its 10 day use.

A check was made to determine if any difference in flow rate occurred for using the metal diaphram pump (section A.3.3) versus a pressurized air source. This was investigated because of the pulsed output of all diaphram pumps. No difference was seen for the two sources.

Because mass flow meters are sensitive to moisture, a $CaSO_4$ dryer was incorporated into the ambient air sampling train (Figure A.1). The station zero air is moisture free and hence required no dryer. The $CaSO_4$ in the dryer was changed every two days to preclude any moisture breakthrough.

Many different materials could have been used to remove moisture from the air sample, but many would also have an affinity for CO_2 (e.g. silica gel). Calcium sulfate ($CaSO_4$) and potassium carbonate (K_2CO_3) are two of the most common desiccants that have no affinity for CO_2. To prove this contention a check was made of the amount of oxalic acid needed to neutralize

30 litres of 300 ppm CO_2 (Linde) with and without the sample passing through a $CaSO_4$ dryer. The results are presented in Table A.1 and indicate no CO_2 adsorption by the $CaSO_4$.

A.3.7 QUALITY ASSURANCE

Tests were performed to assess the accuracy and reproducibility of the analyses done for Task Order 121. These tests included absorption efficiency of CO_2, reproducibility of titrations and analyses, and agreement between actual and standard CO_2 concentration results.

A.3.7.1 CO_2 Absorption Efficiency

In the bubbler absorption method of analysis, it is necessary that all of the CO_2 be absorbed in the absorbing solution with none being allowed to pass through. A test was devised to determine if any CO_2 was passing through the CO_2 bubbler unreacted.

Using a Scott-Marrin analyzed tank of 370 $\pm$ 18 ppm CO_2 in air[10], two identical CO_2 bubblers were connected in series and this CO_2 standard sampled at 1 l/min (STP) for 46 min. While a higher CO_2 concentration standard run at 30 min. would have been more desirable, this was the best that could be accomplished using available standards. This standard is comparable to a CO_2 concentration of 580 ppm CO_2 run for 30 minutes. The results are presented in Table A.2 and indicate that no CO_2 passes through the first bubbler. This test only proves that this analytical method is accurate for concentrations up to 580 ppm CO_2 sampled at 1 l/min (STP) for 30 minutes. Any concentration in excess of 580 ppm, sampled at 1 l/min (STP) for 30 minutes would require further checks af absorption efficiency. Note that the maximum theoretical concentration that can be handled using these sampling and analytical procedures[11] is 747 ppm CO_2.

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10. Analyzed at 378 ppm CO_2 by Rockwell personnel.

11. Sample bubbled at 1 l/min (STP) for 30 min. through 100 ml of 0.01 M $Ba(OH)_2$.

A.3.7.2 Reproducibility of Titrations

Prior to any sampling, tests were run to determine if any variations were present in the acid-base titrations used in analyses. The results are presented in Table A.3 and show only a $\pm$ 0.05 ml 0.005 M oxalic acid variation. Later duplicate titrations of sample analyses showed a maximum variation of 0.15 ml corresponding to an error of $\pm$ 3 ppm CO_2.

A.3.7.3 Analysis of Scott-Marrin and NBS CO_2 Standards

Included in Table A.4 are the analyses of the 5 Scott-Marrin CO_2 standards used in this study. As may be seen, these results were within analysis tolerances supplied by Scott. Each analysis was repeated using the analytical procedures described in section A.3.4. The sampling procedure was equivalent to that used for the station zero air (section A.3.3).

A certified CO_2 cylinder was purchased from the National Bureau of Standards (NBS) for a final check of the accuracy of all analytical and sampling procedures. A Bendix portable calibrator was used to generate varying CO_2 concentrations. These CO_2 concentrations were sampled as in section A.3.3 (ambient air samples) and analyzed as in section A.3.4. The relatively low CO_2 maximum concentration (85 ppm) is a function of the limitations of this particular calibrator. As may be seen from Table A.5, the comparability between theoretical and analyzed CO_2 concentrations are very good.

Tables A.4 and A.5 show that each analysis was performed twice. The difference between the two of 2 ppm maximum is less than the 3 ppm maximum shown in section A.3.7.2. This decrease in error may be in part due to improved laboratory techniques and in part to the incorporation of the Brooks mass flow controller (section A.3.6).

A.3.7.4 Analytical Stability with Respect to Sample Volume

During the early part of this Task Order, tests were conducted on the variability of analytical results as a function of sample volume. These tests were done in accordance with all of the sampling (section A.3.3) and analytical methods (section A.3.4), with sample flow controlled using the Tylan mass flow meter. The results are presented in Table A.6. These datum

show good comparative results regardless of sample flow used. The error from this test is ±3 ppm CO_2. The gas used was a Linde CO_2 standard analyzed at 300 ±18 ppm.[12]

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12. Analyzed by Rockwell personnel at 293 ppm CO_2.

TABLE A.1. $CaSO_4$ ADSORPTION OF CO_2 TEST

No $CaSO_4$ Dryer		$CaSO_4$ Dryer	
1st titration	27.80 ml	1st titration	27.70 ml
2nd titration	27.75 ml	2nd titration	27.75 ml

Titrations using 0.005 M oxalic acid.

TABLE A.2. CO_2 ADSORPTION EFFICIENCY

$Ba(OH)_2$ soln. (unreacted)		$Ba(OH)_2$ soln. 2nd bubbler	
1st titration	49.0 ml	1st titration	49.0 ml
2nd titration	49.0 ml	2nd titration	49.0 ml

Titrations using 0.005 M oxalic acid

TABLE A.3. TITRATION REPRODUCIBILITY

Titration #1	36.40 ml oxalic acid
Titration #2	36.45 ml oxalic acid
Titration #3	36.40 ml oxalic acid
*Titration #4	36.40 ml oxalic acid

*14 hours later

$Ba(OH)_2$ conc. → 0.01 M

Oxalic acid → 0.005 M

TABLE A.4. ANALYSIS OF SCOTT-MARRIN CO_2 STANDARDS

Scott CO_2 Standard	Rockwell Analysis Analysis #1	Rockwell Analysis Analysis #2
4.2 ± 0.4 ppm CO_2	4.4 ppm	4.4 ppm
46 ± 2 ppm	47 ppm	46 ppm
92 ± 5 ppm	94 ppm	93 ppm
188 ± 9 ppm	190 ppm	190 ppm
370 ± 18 ppm	379 ppm	377 ppm

TABLE A.5. ANALYSIS OF NBS CO_2 STANDARDS

NBS Standard (listed ± 1%)	Rockwell Analysis Analysis #1	Rockwell Analysis Analysis #2
60 ppm	60 ppm	59 ppm
85 ppm	85 ppm	86 ppm
22.6 ppm	23 ppm	22 ppm

TABLE A.6. SAMPLE VOLUME ANALYSIS TEST

Amount of Sample (STP)	Analysis
10 litres	296 ppm
20 litres	293 ppm
60 litres	290 ppm

REFERENCES

1. Jacobs, M. B., The Chemical Analysis of Air Pollutants, p. 245, 1960, Interscience Publications, Inc.

2. Leithe, W., The Analysis of Air Pollutants, p. 188-194, 1972, Ann Arbor Science Publications, Inc.